DOCKET NO: 274674US0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF	:
OLEG STENZEL, ET AL	: ART UNIT: 1793
SERIAL NO: 10/542,763	:
FILED: JANUARY 17, 2006	: EXAMINER: PARVINI, P.
FOR: HIGHLY DISPERSIBLE SILICA FOR USING IN RUBBER	:

APPEAL BRIEF

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

This is an appeal of the Final Rejection dated October 15, 2008 of Claims 1-9, 16-17 and 21. A Notice of Appeal, along with a two-month extension of time, was timely filed on March 16, 2009.

I. REAL PARTY IN INTEREST

The real party in interest in this appeal is Evonik Degussa GmbH, having an address at Rellinghauser Strasse 1-11, 45128 Essen, Germany.

II. RELATED APPEALS AND INTERFERENCES

Appellants, Appellants' legal representative and the assignee are aware of no appeals or interferences which will directly affect or be directly affected by or have a bearing on the Board's decision in this appeal, except for an appeal in copending Application No. 10/542,850.

III. STATUS OF THE CLAIMS

Claims 1-9, 16-17 and 21 stand rejected and are herein appealed. Claims 10-15, 18 and 22-25 stand withdrawn from consideration. Claims 19 and 20 have been canceled.

IV. STATUS OF THE AMENDMENTS

A response, without amendment, under 37 CFR 1.116, was filed on January 9, 2009. An Advisory Action dated February 11, 2009 indicated that the response did not put the application in condition for allowance.

V. SUMMARY OF THE CLAIMED SUBJECT MATTER

A summary of the claimed subject matter, as claimed in independent Claim 1, is mapped out below, with reference to page and line numbers in the specification added in **[bold]** after each element.

A precipitated silica which has the following physical and chemical properties: **[page 2, lines 25-26]**

CTAB surface area	100-160 m^2/g **[page 2, line 27]**
BET surface area	100-190 m^2/g **[page 2, line 31]**
DBP value	180-300 g/(100 g) **[page 2, line 35]**
Sears value V_2	15-28 ml/(5 g) **[page 2, line 39]**
Moisture level	4-8 % **[page 3, line 5]**
Ratio of Sears value V_2 to BET surface area	0.150 to 0.280 ml/($5m^2$). **[page 3, lines 11-14]**

VI. GROUNDS OF REJECTION

Ground (A)

Claims 1-9, 16-17 and 21 stand rejected under 35 USC 103(a) as unpatentable over US 5,846,506 (Esch et al) in view of US 5,935,543 (Boyer et al).

Ground (B)

Claims 1-9, 16-17 and 21 stand rejected under 35 USC 103(a) as unpatentable over US 6,180,076 (Uhrlandt et al) in view of Boyer et al.

Ground (C)

Claims 1-9, 16-17 and 21 stand provisionally rejected on grounds of obviousness-type double patenting over Claims 1-8, 18, 19, 23 and 30 of copending Application No. 10/542,850 (copending application).

VII. ARGUMENT

Ground (A)

Claims 1-9, 16-17 and 21 stand rejected under 35 USC 103(a) as unpatentable over Esch et al in view of Boyer et al. That rejection is untenable and should not be sustained.

An embodiment of the present invention, as recited in Claim 1, is a precipitated silica which has the following physical and chemical properties:

CTAB surface area	100-160 m^2/g
BET surface area	100-190 m^2/g
DBP value	180-300 g/(100 g)
Sears value V_2	15-28 ml/(5 g)
Moisture level	4-8 %

Ratio of Sears value V_2 to

BET surface area 0.150 to 0.280 ml/(5m^2)

(emphasis added.)

As described in the specification beginning at page 1, line 10, precipitated silicas for use as reinforcing fillers in rubber or elastomer mixtures, such as tires, are known, and that the properties of such silicas are decisively determined by their preparation process. Applicants have discovered that by precipitating at a contain alkali value (AV), they can obtain precipitated silicas having improved properties when used in rubber or elastomer mixtures compared to precipitated silicas made under other precipitation conditions.

While claims drawn to a process of making stand withdrawn in the application, nevertheless, the above-emphasized property, together with the other recited properties, is not believed to be achievable by the processes disclosed by the applied prior art for making their precipitated silicas.

It must be borne in mind that precipitated silicas always have silanol groups on their surfaces. It therefore is readily apparent that the greater the surface area of a silica, the greater the absolute number of the silanol groups. The absolute number of the silanol groups is expressed in terms of the Sears value V_2. The discovery of the present invention is that for the first time, applicants have been successful in increasing the number of silanol groups on a given surface area of a precipitated silica. Stated in other terms, the silica of the present invention, while having a BET surface area which is identical to embodiments of known precipitated silicas, has a higher absolute number of silanol groups. That is, the present precipitated silica has a higher Sears value V_2. Accordingly, in order to eliminate the effect of the surface area of a silica on the silanol number, the ratio of the absolute number of silanol groups to the BET surface area is taken and a normalized, relative group density of silanol

groups is obtained. This normalized number is present in the claims of the invention and is a value of 0.150 to 0.280 ml/(5m^2), as above emphasized.

The importance of the silanol groups on the surface of the silica is described in the paragraph that bridges pages 13 and 14 of the specification. The silanol groups can react with a coupling reagent such as bis(3-triethoxysilylpropyl)tetrasulfane while another portion of the coupling molecule reacts with the rubber matrix material, thereby achieving bonding of the silica to the rubber matrix. The greater the number of silanol groups, the greater the degree of coupling between the silica and the coupling reagent. This greater degree of coupling increases the bonding of the silica particles to the rubber matrix, thereby resulting in a greater reinforcement potential. The Sears value V_2 is a factor which permits a description of the number of silanol groups in the silica. On the other hand, the BET surface area of a silica is its specific surface area, which has a major effect on the processing behavior of a compounded material, and on the material's other properties after vulcanization. However, the absolute number of silanol groups is not itself sufficient for adequate characterization of a precipitated silica, because precipitated silicas with a high surface area generally have a higher absolute number of silanol groups than precipitated silicas with a low surface area, as discussed above. The important factor is therefore the quotient that is calculated by dividing the Sears value V_2 by the BET surface area. In this way it is possible to represent the reinforcement potential generated via the silanol groups per unit of specific surface area introduced.

In addition, Applicants wish to emphasize an important understanding that must be given to precipitated silicas that are to be used as fillers in the preparation of rubber materials, particularly fillers that are to be used in the construction of tire treads, that has long been known to those of skill in the art, and is described in US 5,929,156 (Fultz et al) at column 3, lines 46-54, as follows:

> It is well known that a single physical characteristic, such as surface area or particle size, does little to describe a silica product or to predict is behavior in a specific application. The mechanisms which govern how a particular silica product performs in a given end-use can be extraordinarily complex and are often not well understood; thus, linking one or even a few conventionally-measured silica product physical properties to particular end-use performance characteristics is extremely difficult and potentially misleading.

Accordingly, in the present application, Applicants have found that a particular precipitated silica having the particular surface area and other surface characteristics as described is uniquely exceptional in its ability to function as a reinforcing filler in tire tread formulations. Thus, the different value ranges of BET, CTAB, DBP value, Sears value, moisture level and Sears value/BET ratio are distinctive in describing a successful precipitated filler for tire tread formulations.

Esch et al discloses a precipitated silica having, *inter alia*, a BET surface of 35 to 350 m^2/g and a silanol group density V_2, i.e., Sears value, of 6 to 20 ml[/(5 g)] (column 1, line 46ff). Esch et al discloses preparing their precipitated silica by, in effect, maintaining a constant pH (column 2, line 28 ff).

Boyer et al is relied for a disclosure of a precipitated silica having a particular moisture level.

The Examiner holds that it would have been obvious to modify Esch et al in order to achieve a moisture level of 4-8% in view of Boyer et al. In so holding, the Examiner finds that the Sears value/BET ratio range in Esch et al is from about 0.017 to about 0.57 (by calculating ratios from the end points of the respective ranges for Sears value and BET ratio, i.e., 6/350 and 20/35), and thus, the recited range herein of 0.150 to 0.280 ml/($5m^2$) would have been obvious.

While the above ratio range was correctly calculated by the Examiner, the relevant disclosure must be evaluated as a person of ordinary skill in the art would. Such a person would appreciate that the greater the BET ratio, the greater the expected Sears value. Indeed,

the table at column 2 of Esch et al confirms this, which table shows increasing Sears value range with increasing BET surface area range. Thus, it is submitted that one of ordinary skill in the art would **not** interpret Esch et al as describing as part of their invention a Sears value/BET ratio range of from about 0.017 to about 0.57. The three precipitated silica examples (Examples 1 to 3) therein are consistent with this notion. The following table shows the calculated Sears value/BET ratio of each of the examples.

	Sears Value (V_2)	BET	V_2/BET ratio
Example 1	9.0	80	0.113
Example 2	9.1	120	0.076
Example 3	15.7	184	0.085
Present Claim 1			0.150 - 0.280

The data in the table show that none of the examples of Esch et al have a V_2/BET ratio value that falls within the range specified in the present claims. In fact, the ratio values of the examples of Esch et al are all lower by at least 25 % of the minimum of the presently claimed range. In other words, the silicas of Esch et al are characterized by much fewer OH groups per square meter of surface area. Thus, the silica of Esch et al is not that of the present invention.

In addition, Example 5 of Esch et al compares Sears values for two BET ratio ranges of their examples with some commercially available precipitated silicas. Indeed, the Sears value/BET ratio shown in Example 5 is actually lower for Esch et al's examples than for the commercially available precipitated silicas, yet all were far below the presently-recited minimum of 0.150.

Additional improved effects of the invention are an improved dispersion behavior and vulcanization times, as described in the specification at page 4, lines 15-17, and as described in the specification by the vulcanizate data in Tables 2.4 and 2.8 and the description thereinafter at page 39, line 19 to page 40, line 3, and page 44, lines 3 to 14, respectively. The reference example in Table 2.5 at page 40, where the composition contains Ultrasil 3370 GR, is Example 3 of Esch et al. Thus, a direct comparison of Esch et al with Example 2.2 of the present invention is provided.

While Applicants are cognizant of precedent that a prior art patent is not limited to its examples, nevertheless, there is no indication in Esch et al of any appreciation of the significance of Sears value/BET ratio, and thus no motivation to optimize it. Thus, the Examiner has not shown that the prior art was aware that Sears value/BET ratio is a result-effective variable. Thus, the present claims are patentable under the rationale of *In re Antonie*, 559 F.2d 618, 195 USPQ 6, 8-9 (CCPA 1977) (exceptions to rule that optimization of a result-effective variable is obvious, such as where the results of optimizing the variable are unexpectedly good or where the variable was not recognized to be result effective). Applicants are entitled to prevail under either of the above exceptions.

Nor does Esch et al provide enablement for how to prepare precipitated silicas of higher Sears value/BET ratios than the prior art.

In addition, the Declaration under 37 CFR 1.132 of Andre Wehmeier, filed June 27, 2008 (Wehmeier Declaration), which compares present Example 1.5 (having a V_2/BET ratio of 0.227 ml/5 m^2) to Example 3 of Esch et al (having a V_2/BET ratio of 0.085 ml/5 m^2), provides further evidence of superiority over Esch et al. It is submitted that Example 3 of Esch et al is the closest prior art thereof. Wehmeier concludes at paragraph (6) that the data in the Table 4 therein show a better Mooney viscosity M_L value in the MDR test. This indicates a superior processing property of the compounded rubber material within the scope

of the present invention. Desirably, the vulcanization time t 90 % and the vulcanization rate t 80 % - t 20 % are drastically reduced over the values of the compared composition of Esch et al. These greatly improved raw-mixture properties can be attributed, in particular, to the higher and better ratio of Sears number to BET surface area, since faster and more effective hydrophobing, and consequently greater binding capacity of the silane to the silica is possible. The greatly improved properties of the vulcanized derivative can also be attributed for the most part to this analytical characteristic. For example, the improved binding of the silica leads to better reinforcement of the vulcanized derivative in the tension test, as can be observed in the higher value of Modulus 200 % and the higher Modulus 200 %/50 % reinforcement factor. As a consequence, the DIN abrasion is improved by more than 18 %. The hysteresis behavior, which correlates directly with the rolling resistance of a tire that is finished with the present running-surface compound, can also be improved simultaneously by more than 18 % with the precipitated silica of the invention (see tan δ, 60° C). This improvement is also confirmed by the ball rebound value at 70° C.

The deficiencies of Esch et al are neither overcome nor improved upon by Boyer et al. As discussed above, Boyer et al is applied only for its disclosure of moisture level. But Boyer et al discloses and suggests nothing regarding Sears value (V_2)/BET ratio.

Claim 4

Claim 4 is separately patentable. Esch et al discloses Sears values of 8-19 for BET values from 100-200 m^2/g (column 2, lines 12-20). Claim 4 recites a minimum Sears value of 20.

Claim 5

Claim 5 is separately patentable. Esch et al discloses Sears values of 8-19 for BET values from 100-200 m^2/g (column 2, lines 12-20). Claim 4 recites a minimum Sears value of 22.

Claim 8

Claim 8 is separately patentable. The minimum Sears value of 0.170 is even further away from Esch et al than the minimum Sears value of 0.150 in Claim 1.

For all the above reasons, it is respectfully requested that this rejection be REVERSED.

Ground (B)

Claims 1-9, 16-17 and 21 stand rejected under 35 USC 103(a) as unpatentable over Uhrlandt et al in view of Boyer et al. That rejection is untenable and should not be sustained.

Uhrlandt et al discloses a precipitated silica having, *inter alia*, a BET surface area of 120 to 200 m^2/g and a silanol group density V_2, i.e., Sears value, of 6 to 25 ml[/(5 g)] (column 1, line 41ff). Uhrlandt et al discloses preparing their precipitated silica by, in effect, maintaining a constant pH (column 2, line 20 ff), like Esch et al.

Aside from differences in the BET and Sears value ranges, Uhrlandt et al is deficient for substantially the same reasons as Esch et al. Thus, the comments and arguments as presented above with respect to the combination of Esch et al and Boyer et al apply equally as well to the combination of Uhrlandt et al and Boyer et al, which comments and arguments are hereby incorporated by reference.

For all the above reasons, it is respectfully requested that this rejection be REVERSED.

Ground (C)

Claims 1-9, 16-17 and 21 stand provisionally rejected on grounds of obviousness-type double patenting over Claims 1-8, 18, 19, 23 and 30 of copending Application No. 10/542,850 (copending application). Pursuant to M.P.E.P. 822.01, the Examiner is respectfully requested to hold the rejection in abeyance until the present claims are found to be allowable but for this rejection or the copending application has been patented.

VIII. CONCLUSION

For the above reasons, it is respectfully requested that the rejections be REVERSED.

Respectfully submitted,

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CLAIMS APPENDIX

Claim 1. A precipitated silica which has the following physical and chemical properties:

CTAB surface area	100-160 m^2/g
BET surface area	100-190 m^2/g
DBP value	180-300 g/(100 g)
Sears value V_2	15-28 ml/(5 g)
Moisture level	4-8 %
Ratio of Sears value V_2 to BET surface area	0.150 to 0.280 ml/($5m^2$).

Claim 2. The precipitate silica as claimed in claim 1, wherein the BET surface area ranges from 100 to 170 m^2/g.

Claim 3. The precipitated silica as claimed in claim 1, wherein the CTAB surface area ranges from 100 to 150 m^2/g.

Claim 4. The precipitated silica as claimed in claim 1, wherein the Sears value V_2 ranges from 20 to 28 ml/(5 g).

Claim 5. The precipitated silica as claimed in claim 1, wherein the Sears value V_2 ranges from 22 to 28 ml/(5 g).

Claim 6. The precipitated silica as claimed in claim 1, wherein the DBP value ranges from 200 to 250 g/(100 g).

Claim 7. The precipitated silica as claimed in claim 1, wherein the DBP value ranges from 250 to 280 g/(100 g).

Claim 8. The precipitated silica as claimed in claim 1, wherein the ratio of Sears value V_2 to the BET surface area ranges from 0.170 to 0.280 ml/(5 m^2).

Claim 9. The precipitated silica as claimed in claim 1, wherein the BET/CTAB ratio ranges from 0.9 to 1.2.

Claim 16. The precipitated silica claimed in claim 1, wherein the surface of the precipitated silica is modified with organosilanes of the formulae I to III

$[SiR^1_n(OR)_r(Alk)_m(Ar)_p]_q[B]$ (I),

$SiR^1_n(OR)_{3-n}(Alkyl)$ (II),

or

$SiR^1_n(OR)_{3-n}(Alkenyl)$ (III),

where

B is -SCN, -SH, -Cl, $-NH_2$, $-OC(O)CHCH_2$, $-OC(O)C(CH_3)CH_2$ (if q = 1), or $-S_w-$ (if q = 2), B being chemically bonded to Alk, R and R^1, which are identical or different, are each an aliphatic, olefinic, aromatic, or arylaromatic radical having 2-30 carbon atoms, optionally substituted by at least one of the following groups: hydroxyl, amino, alcoholate, cyanide, thiocyanide, halo, sulfonic acid, sulfonic ester, thiol, benzoic acid, benzoic ester, carboxylic acid, carboxylic ester, acrylate, methacrylate, or organosilane;

n is 0, 1, or 2;

Alk is a bivalent unbranched or branched hydrocarbon radical having from 1 to 6 carbon atoms;

m is 0 or 1;

Ar is an aryl radical having from 6 to 12 carbon atoms, which may be substituted by one of the following groups: hydroxyl, amino, alcoholate, cyanide, thiocyanide, halo, sulfonic acid, sulfonic ester, thiol, benzoic acid, benzoic ester, carboxylic acid, carboxylic ester, acrylate, methacrylate or organosilane radical;

p is 0 or 1, with the proviso that p and n are not simultaneously 0;

q is 1 or 2;

w is a number from 2 to 8;

r is 1, 2, or 3, with the proviso that $r + n + m + p = 4$;

Alkyl is a monovalent unbranched or branched saturated hydrocarbon radical having from 1 to 20 carbon atoms,

Alkenyl is a monovalent unbranched or branched unsaturated hydrocarbon radical having from 2 to 20 carbon atoms.

Claim 17. The precipitated silica as claimed in claim 1, wherein the surface of the precipitated silica is modified with organosilicon compounds whose composition is

$SiR^2_{4-n}X_n$ (where n = 1, 2, 3, 4),

$[SiR^2_xX_yO]_z$ (where $0 \leq x \leq 2$; $0 \leq y \leq 2$; $3 \leq z \leq 10$, where $x + y = 2$),

$[SiR^2_xX_yN]_z$ (where $0 \leq x \leq 2$; $0 \leq y \leq 2$; $3 \leq z \leq 10$, where $x + y = 2$),

$SiR^2_nX_mOSiR^2_oX_p$ (where $0 \leq n \leq 3$; $0 \leq m \leq 3$; $0 \leq o \leq 3$; $0 \leq p \leq 3$, where $n + m = 3$, $o + p = 3$),

$SiR^2_nX_mNSiR^2_oX_p$ (where $0 \leq n \leq 3$; $0 \leq m \leq 3$; $0 \leq o \leq 3$; $0 \leq p \leq 3$, where $n + m = 3$, $o + p = 3$), and/or

$SiR^2_nX_m[SiR^2_xX_yO]_zSiR^2_oX_p$ (where $0 \leq n \leq 3$; $0 \leq m \leq 3$; $0 \leq x \leq 2$; $0 \leq y \leq 2$; $0 \leq o \leq 3$; $0 \leq p \leq 3$; $1 \leq z \leq 10{,}000$, where $n + m = 3$, $x + y = 2$, $o + p = 3$) where

R^2 is alkyl and/or aryl radicals, substituted and/or unsubstituted, having from 1 to 20 carbon atoms, and/or is alkoxy and/or alkenyl and/or alkynyl groups, and/or is sulfur-containing groups,

X is a silanol, amino, thiol, halogen, alkoxy, alkenyl and/or hydrogen radical.

Claim 21. (Previously Presented) A vulcanizable rubber mixture or a vulcanizate whose filler component comprises the precipitated silica as claimed in claim 1 which has the following physical and chemical properties:

CTAB surface area	100-160 m^2/g
BET surface area	100-190 m^2/g
DBP value	180-300 g/(100 g)
Sears value V_2	15-28 ml/(5 g)
Moisture level	4-8%
Ratio of Sears value V_2 to BET surface area	0.150 to 0.280 ml/(5 m^2).

EVIDENCE APPENDIX

Declaration under 37 CFR 1.132 of Andre Wehmeier, filed June 27, 2008.

US 5,929,156 (Fultz et al), cited in a response filed January 7, 2009.

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FOR: HIGHLY DISPERSIBLE SILICA FOR USING IN RUBBER	:

DECLARATION UNDER 37 CFR 1.132

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

Now comes ANDRE WEHMEIER who deposes and says that:

(1) I am an inventor of the above-identified invention.

(2) Since 1998 I have been employed by EVONIK as a researcher engaged in the study of PRECIPITATED SILICAS AND RUBBER REINFORCEMENT.

(3) I have considered the Office Action of March 4, 2008 and the Esch et al and Boyer et al patents cited therein.

(4) The following information provides details of the preparation of the vulcanizable rubber composition of Example 3 of the Esch et al patent of record and a vulcanized rubber product prepared therefrom. Also provided are data involving the same tests for the rubber embodiment of the present invention identified as Example 1.5 on pages 33 *et seq* of the specification.

(5) Table 1 below provides the details of the mixing of ingredients for the preparation of a vulcanizable rubber formulation. The details of the mixture of ingredients are also provided by the "reference" formulation in Table 2.5 on page 40 of the specification. In the table, the abbreviation "phr" means parts by weight relative to 100 parts by weight of the raw rubber used.

Table 1

Substance	phr	Article designation	Company
1^{st} step	**Basic mixing**		
Buna VSL 5025-1	96.0	S-SBR; oil-extended	Lanxess Europe GmbH & Co. KG; 51369 Leverkusen; Germany
Buna CB 24	30.0	cis-1,4-BR	Lanxess Europe GmbH & Co. KG; 51369 Leverkusen; Germany
Silica	80.0		
X 50-S	12.8	Si 69 (bis(3-triethoxysilylpropyl)tetrasulfane) / carbon black of type N 330: 50% / 50%	Evonik Degussa GmbH; 45128 Essen; Germany
ZnO; RS RAL 844 C	3.0	ZnO	Amsperger Chemikalien GmbH; 50858 Cologne; Germany
EDENOR ST1 GS	2.0	Palmitic-stearic acid; "iodine number 1" stearin	Caldic Deutschland GmbH & Co. KG' 40231 Düsseldorf; Germany
Naftolen ZD	10.0	Aromatic plasticizer oil	Chemetall GmbH; 60487 Frankfurt a. Main; Germany
Vulkanox 4020 / LG	1.5	N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)	Rhein Chemie Rheinau GmbH; 68219 Mannheim Rheinau; Germany
Protektor G 3108	1.0	Mixture of refined hydrocarbon waxes	Paramelt BV; 706875 Paramelt BV; NL 1704 RJ Heerhugowaard; The Netherlands
2^{nd} step	**Lasting / remill step**		
Step 1 batch			
3^{rd} step	**Finish mixing**		
Step 2 batch			
Vulkacit D	2.0	N,N'-Diphenylguanidine (DPG)	Rhein Chemie Rheinau GmbH; 68219 Mannheim Rheinau; Germany
Vulkacit CZ/EG-C	1.5	N-Cyclohexyl-2-benzothiazole sulfenamide (CBS)	Rhein Chemie Rheinau GmbH; 68219 Mannheim Rheinau; Germany
Perkacit TBZTD	0.2	Tetrabenzylthiuram disulfide (TBzTD)	Flexsys N.V./S.A., Woluwe Garden; B-1932 St. Stevens Woluwe; Belgium
Ground sulfur	1.5	Finely divided sulfur according to Ph Eur, BP	Merck KGaA; 64271 Darmstadt; Germany

The general method for manufacturing rubber mixtures and their vulcanized derivatives is described in the "Rubber Technology Handbook" by W. Hofmann, Hanser Verlag, 1994. The specific mixing conditions for the composition described in Table 1 above are specified in the following Table 2.

Table 2

1st step	Brabender 350 S mixer, filling level 0.73, 70 rpm, chamber temperature 70 °C, friction 1 : 1.11 plunger pressure 5 bar
0.0 to 0.5 minutes 0.5 to 1.5 minutes 1.5 minutes 1.5 to 2.5 minutes 2.5 minutes 2.5 to 3.5 minutes 3.5 minutes 3.5 to 5.0 minutes 5.0 minutes	Polymers 1/3 silica, X 50-S Clean 1/3 silica Clean 1/3 silica, ZnO, stearic acid, oil, Vulkanox 4020, Protektor Clean Mix; with speed variation if necessary, in order to reach the ejection temperature Discharge batch (batch temperature 145 °C to 155 °C) and distribute on roll: Cut in and fold over 3 * on left, 3 * on right, turn over 5 * for narrow roll nip, 5 * for broad roll nip Draw out a rolled sheet
24 hours intermediate storage at room temperature to step 2	
2nd step	Brabender 350 S mixer, filling level 0.71, 80 rpm, chamber temperature 80 °C, friction 1 : 1.11 plunger pressure 5 bar
0.0 to 2.0 minutes 2.0 to 5.0 minutes 5.0 minutes	Plasticize batch from step 1 Maintain batch temperature at 150 °C by speed variation Discharge batch (batch temperature 145 °C to 155 °C) and distribute on roll: Cut in and fold over 3 * on left, 3 * on right, turn over 5 * for narrow roll nip, 5 * for broad roll nip Draw out a rolled sheet
4 hours intermediate storage at room temperature to step 3	
3rd step	Brabender 350 S mixer, filling level 0.69, 50 rpm, chamber temperature 60 °C, friction 1 : 1.11 plunger pressure 5 bar
0.0 to 0.5 minutes 0.5 to 2.0 minutes 2.0 minutes	Batch from step 2 Constituents of the 3rd step Discharge batch (batch temperature 90 °C to 110 °C) and distribute on roll: Cut in and fold over 3 * on left, 3 * on right, turn over 5 * for narrow roll nip, 5 * for broad roll nip Draw out a rolled sheet in the thickness necessary for preparation of the test specimens
12 hours intermediate storage at room temperature until vulcanization of the test specimens	

Table 3 below identifies the standard test procedures employed in order to determine the values of the physical properties of the vulcanized rubber composition of Example 3 of the Esch et al patent.

Table 3

Physical testing	Standard / Conditions
ML (1+4), 100 °C, 3rd step (MU)	DIN 53523/3 ISO 667
Vulcameter test, temperature, 165 °C, deflection 0.5 ° MDR rheometer M_L (dNm) t 90% (minutes) t 80% - t 20% (minutes)	DIN 53529/3 ISO 6502
Tensile test on bar S 1, 23 °C (median values from 3 bars) Modulus 200% (MPa) Modulus 200% / modulus 50% (–)	DIN 53504, ISO 37
Ball rebound 70 °C (%)	DIN EN ISO 8307, drop height 500 mm, steel ball, d = 19 mm, 28 g
DIN abrasion, 23 °C, 10 N force (mm^3)	DIN 53516
Viscoelastic properties, 50 N preliminary force and 25 N amplitude force, 16 Hz Temperature equilibration time 5 minutes, recording of measured values after 30 s of test time tan δ, 60 °C (–)	DIN 53513, ISO 2856

Table 4 below presents the data obtained for the measured property values identified in Table 3 above.

Table 4

		US 5846506 Example 3	OZ 6287 Example 1.5
ML (1+4), 100 °C, 3rd step	MU	90	88
MDR: 165 °C; 0.5 °			
M_L	dNm	3.5	2.8
t 90%	min	9.7	6.4
t 80% - t 20%	min	3.2	2.1
Vulcanization time (165 °C)	min	20	20
Modulus 200%	MPa	8.0	11.9
Modulus 200% / modulus 50%	–	5.0	7.4
DIN abrasion; 10 N	mm^3	77	63
Ball rebound; 70 °C	%	65.8	69.3
Zwick: 16 Hz; 50 N ± 25 N			
tan δ, 60 °C	--	0.134	0.109

(6) It is clear from the data presented in Table 4 above that the compound rubber material of Example 1.5 of the present invention exhibits a profile of superior rubber values in comparison to the compound rubber material of Example 3 of the Esch et al patent which is based on a precipitated silica having a Sears number (V_2)/ BET ratio (0.085 ml/($5m^2$) outside the range of 0.150 to 0.280 ml/($5m^2$) that is presently claimed for the silica of the invention. The data in the table above show a better Mooney viscosity M_L value in the MDR test. This indicates a superior processing property of the compounded rubber material within the scope of the present invention. Desirably, the vulcanization time t 90 % and the vulcanization rate t 80 % - t 20 % are drastically reduced over the values of the compared composition of Esch et al. These greatly improved raw-mixture properties can be attributed, in particular, to the higher and better ratio of Sears number to BET surface area, since hereby faster and more effective hydrophobing, and consequently greater binding capacity of the silane to the silica is possible. The greatly improved properties of the vulcanized derivative

can also be attributed for the most part to this analytical characteristic. For example, the improved binding of the silica leads to better reinforcement of the vulcanized derivative in the tension test, as can be observed in the higher value of Modulus 200 % and the higher Modulus 200 %/50 % reinforcement factor. As a consequence, the DIN abrasion is improved by more than 18 %. The hysteresis behavior, which correlates directly with the rolling resistance of a tire that is finished with the present running-surface compound, can also be improved simultaneously by more than 18 % with the precipitated silica of the invention (see tan δ, 60° C). This improvement is also confirmed by the ball rebound value at 70° C (0.109).

(7) The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

(8) Further deponent says not.

25.06.2008

(Date)

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United States Patent [19]

Fultz et al.

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[45] Date of Patent: *Jul. 27, 1999

[54] SILICA PRODUCT FOR USE IN ELASTOMERS

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[*] Notice: This patent is subject to a terminal disclaimer.

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[51] Int. Cl.^{6} C08K 3/00

[52] U.S. Cl. 524/492; 423/335; 524/493

[58] Field of Search 524/492, 493; 423/335

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[57] ABSTRACT

A precipitated amorphous silica product particularly useful as a highly dispersible filler to elastomeric compounds, especially rubber passenger tire tread formulations. The invention has a CTAB specific surface area of about 10 m^2/g to less than 140 m^2/g; a multi-point BET surface area of about 50–261 m^2/g; a 5% pH value of about 5.0–8.5; a DBP oil absorption of about 160–310 $cm^3/100$ g; a linseed oil absorption of about 150–300 $cm^3/100$ g; a projected surface area of no greater than about 4000 nm^2; and a pore volume ratio of pores ranging from 175 to 275 Å in diameter to all pores less than 400 Å in diameter of about 10% to less than 50%.

37 Claims, No Drawings

SILICA PRODUCT FOR USE IN ELASTOMERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a novel precipitated silica product and a process for making the same. More specifically, the invention relates to an amorphous precipitated silica product which is useful as an additive in elastomeric formulations used for formed products, particularly rubber passenger tire treads.

2. Description of the Related Art

As disclosed in Kirk-Othmer, *Encyclopedia of Chemical Technology*, Third Edition, Volume 20, John Wiley Sons, New York, p. 779 (1982), precipitated silica product is used, inter alia, as a filler for rubber. In general, fillers are used as reinforcing agents to improve the mechanical properties of rubber and other elastomers.

Any filler used in elastomeric applications should be easy to handle and easy to formulate into elastomeric mixtures. In powder form, silica products can be difficult to handle because of poor flow and high dust generation. Also, the low bulk density of powder silica products impedes incorporation into elastomers.

While formed silica products can obviate these shortcomings to a certain extent, dispersion of the formed silica product in the elastomer can be difficult, and the degree of reinforcement achieved may be less than would be attained with a powdered silica product. Optimum reinforcing properties are generally achieved when the silica product is homogeneously dispersed throughout the elastomer matrix in a finely-divided state. Therefore, an ideal formed silica product should readily combine with the elastomer matrix and thereafter deagglomerate or disintegrate into a fine powder in the matrix, said fine powder being readily dispersible to a homogeneous state.

In addition, a silica filler should minimize the need for expensive coupling agents in the rubber formulation. Coupling agents are typically tri-alkoxy silanes possessing an amino, mercapto, polysulfidic or other functional group, and are used to reduce heat buildup/hysteresis and to enhance the mechanical improvements provided by the silica filler.

In the case of rubber formulations for the tire industry, and in particular solution styrene-butadiene rubber (s-SBR) for passenger tire treads, there are several desirable yet contradictory rubber tread properties which are strongly affected by the physical properties of the filler employed. The ability of the tread to adhere to the ground whether the surface is dry, wet, snow-covered or ice-covered is very important, and there are known silica fillers which can provide good tire traction under various conditions. However, known traction-enhancing silica fillers do not simultaneously provide the reduced rolling resistance, low tread wear rate and limited structural deformation also demanded of tires. Similarly, silica fillers which improve the rolling characteristics and durability of tire treads have historically done so at the expense of traction, and have typically required high loadings of expensive coupling agents to boost traction. Moreover, known highly-dispersible silica fillers for rubber fail to enhance the processability of rubber.

Consequently, there has been much effort in the silica filler/passenger tire tread formulation art to develop a highly-dispersible silica filler which provides an optimized combination of these contradictory tread properties while enhancing processability. See, e.g., U.S. Pat. Nos. 5,089,554, 5,227,425 and 5,403,570, as well as International Application Nos. WO 95/09127 and WO 95/09128. However, these efforts have at best resulted in unsatisfactory compromises between highly desirable characteristics. Thus, there remains a long-felt need in the art for a highly-dispersible silica filler which, when incorporated into rubber compounds, particularly rubber blends of solution SBR with one or more additional polymers, provides enhanced processability, low rolling resistance, high durability, high all-weather traction and reduced coupling agent demand for passenger tire treads fashioned therefrom or other rubber/elastomer dynamic applications.

OBJECTS OF THE INVENTION

Accordingly, it is an object of the invention to provide a highly-dispersible precipitated amorphous silica product suitable as a filler for elastomeric compounds.

It is another object of the invention to provide an improved highly-dispersible precipitated amorphous silica filler for passenger tire tread applications.

Other objects will become apparent from the description of the invention which follows.

SUMMARY OF THE INVENTION

Briefly, the invention is a precipitated amorphous silica product having a CTAB specific surface area of about 10 m^2/g to less than 140 m^2/g, preferably about 10–110 m^2/g, and more preferably about 10 m^2/g to less than 100 m^2/g; a multi-point BET surface area of about 50–261 m^2/g; a 5% pH value of about 5.0–8.5; a DBP oil absorption of about 160–310 $cm^3/100$ g; a linseed oil absorption of about 150–300 $cm^3/100$ g; a projected surface area of no greater than about 4000 nm^2, preferably no greater than about 3500 nm^2; and a pore volume ratio of pores ranging from 175 to 275 Å in diameter to all pores less than 400 Å in diameter of about 10% to less than 50%.

Preferably, the precipitated amorphous silica product of the invention is subjected to a forming process such as granulation, pelletization, nozzle spray drying and the like. When formed, the invention preferably has a bulk (pour) density of about 0.16–0.30 g/mL, more preferably about 0.16–0.27 g/mL, and a minus 200 mesh content of no greater than about 20 wt %, more preferably no greater than about 10 wt %.

The method of the invention involves adding an acid at a substantially constant rate to a water and alkaline metal silicate mixture, the mixture being at a temperature of about 60–90° C., and the silicate having a mole ratio of about 2.4–3.3. When the pH of the reaction mixture reaches about 10.0–6.5, preferably about 7.8–7.5, more silicate is added together with the acid. The reaction mixture pH is maintained at about 10.0–6.5, preferably about 7.7–7.3 by adjusting the acid addition rate. The silicate addition is discontinued after about 0–60 minutes, preferably about 30 minutes, while the acid addition continues until a reaction mixture pH of about 4.5–6.5, preferably about 5.1–5.5 is achieved. The reaction mixture digests for about 0–60 minutes at a temperature of about 60–99° C., after which the pH is readjusted with acid to about 4.5–6.5, preferably to about 5.1–5.5. An electrolyte, preferably sodium sulfate, may be added at any point in the synthesis through digestion. The silica slurry is filtered from the reaction mixture and washed. Washing is preferably performed until the sodium sulfate content of the washed silica product is no greater than about 4.5%. Preferably, the pH of the washed silica slurry is readjusted to about 6.0–7.0 with acid. The washed silica slurry is then dried, preferably to an H_2O content of no greater than about 8%.

The invention encompasses an elastomeric formulation containing the precipitated amorphous silica product or formed silica product described herein. The elastomer is preferably s-SBR, more preferably s-SBR and at least one other polymer. The other polymer is preferably a diene. The invention also encompasses an elastomer formulation which may be used in a tire tread containing the precipitated amorphous silica product or formed silica product described herein.

DETAILED DESCRIPTION OF THE INVENTION

We have discovered a highly-dispersible silica product which, when incorporated into rubber compounds as a filler in passenger tire tread production, provides a combination of enhanced processability, rolling resistance, durability and traction to the tread product at levels unknown in the prior art. More particularly, the invention provides a unique combination of advantages which were previously considered mutually exclusive; i.e., excellent rubber processing, low rolling resistance, good wet traction, good ice traction, enhanced rubber extrusion, minimal coupling agent demand, good abrasion resistance, and high tensile and modulus. When formed, the invention is also easy to handle and produces minimal dust.

The inventive silica product possesses a unique combination of several physical properties, specifically a CTAB specific surface area of about 10 m^2/g to less than 140 m^2/g, preferably about 10–110 m^2/g, and more preferably about 10 m^2/g to less than 100 m^2/g; a multi-point BET surface area of about 50–261 m^2/g; a 5% pH value of about 5.0–8.5; a DBP oil absorption of about 160–310 $cm^3/100$ g; a linseed oil absorption of about 150–300 $cm^3/100$ g; a projected surface area of no greater than about 4000 nm^2, preferably no greater than about 3500 nm^2; and a pore volume ratio of pores ranging from 175 to 275 Å in diameter to all pores less than 400 Å in diameter of about 10% to less than 50%.

When formed, the invention preferably exhibits a bulk (pour) density of about 0.16–0.30 g/mL, more preferably 0.16–0.27 g/mL, and preferably a minus 200 mesh content of no greater than about 20 wt %, more preferably no greater than about 10 wt %. Granulation, pelletization, and/or other known forming means can be used. The formed silica product of the invention generates less dust, is easy to handle and will readily combine with elastomeric formulations.

It is well known that a single physical characteristic, such as surface area or particle size, does little to describe a silica product or to predict its behavior in a specific application. The mechanisms which govern how a particular silica product performs in a given end-use can be extraordinarily complex and are often not well understood; thus, linking one or even a few conventionally-measured silica product physical properties to particular end-use performance characteristics is extremely difficult and potentially misleading. What we have discovered is that the invention quite unexpectedly performs far better in passenger tire tread applications than known precipitated amorphous silica products having some similar conventionally-measured physical properties, as clearly demonstrated by the tests which we have performed and describe herein. We do not rule out the possibility that novel silica product measuring techniques may be developed which could reveal additional physical distinctions between the invention and the prior art to further explain the significant and surprising performance advantages provided by the invention.

The method of the invention involves adding acid to a mixture of water and an alkaline metal silicate at about 60–90° C. The water and/or silicate can be heated separately or after they are combined. The alkaline metal silicate used is not particularly limited, and can include meta- and di-silicates of any alkali metal or alkaline earth metal. The silicate preferably has a mole ratio of about 2.4–3.3, and is preferably added as an aqueous solution having a silicate concentration of about 10.0–30.0%. An electrolyte may also be added to the reaction medium or combined with one or more of the reactants before or as they are added to the reaction medium. An electrolyte may also be added anytime during the synthesis process through digestion, preferably in the first half of the reaction. Any known electrolyte may be used, with sodium sulfate being preferred.

The acid addition is conducted at a substantially constant rate. The acid is preferably added as a solution of about 5.0–30.0%. Sulfuric acid is preferably used, but other acids such as H_3PO_4, HNO_3, HCl, HCO_2H, CH_3CO_2H and carbonic acid may be successfully employed.

When the pH of the reaction mixture reaches about 10.0–6.5, preferably 7.8–7.5, more silicate is added to the reaction mixture while the acid addition continues. Precipitation occurs during the simultaneous addition, and the precipitation pH is maintained at about 10.0–6.5, preferably at about 7.7–7.3 by adjusting the acid addition rate. The silicate addition is discontinued after about 0–60 minutes, while the acid addition continues until a reaction mixture pH of about 4.5–6.5, preferably about 5.1–5.5 is achieved.

After terminating the acid addition, the reaction mixture is allowed to digest for about 0–60 minutes at a temperature of about 60–99° C. An electrolyte, such as sodium sulfate, may be added at any point in synthesis through the digestion step. After digestion, the reaction mixture pH is readjusted with acid to about 4.5–6.5, preferably to about 5.1–5.5.

The product silica slurry is then filtered from the reaction mixture and washed. Filtration as used herein includes any separation means known in the art, such as rotary filtration, press filtration, pressure filtration, plate and frame filtration, and others. The washing is performed preferably until the sodium sulfate content is less than about 4.5%. Before drying, the pH of the washed silica slurry is preferably readjusted to about 6.0–7.0 with acid.

The washed silica slurry is then dried to a silica product. Drying can be accomplished by wheel spray drying, nozzle spray drying, flash drying, rotary drying, or any other drying means known in the art. Preferably, drying is performed until the moisture content of the silica product is about 8% or less.

The silica product can then, if desired, be placed in a low dust/readily dispersible form by any forming process such as granulation, pelletization, and/or other known forming means. A granulation process is preferred where the silica product is compressed into compacted bodies, the bodies then being broken into smaller particles. The fine fraction of the smaller particles is then recovered and mixed with more silica product, and that mixture is compressed into denser compacted bodies. The denser compacted bodies are then broken-up and screened to the desired size to form the granulated product. A vacuum may be applied during various points in the process to aid in the densification. Spray dried silica can be milled prior to granulation. These forming procedures can be accomplished with or without the aid of other agents, such as water, corn syrup, etc.

As demonstrated below, elastomeric compounds containing the inventive silica product, particularly tire tread compounds, exhibit improved processability and a combination of performance characteristics unknown in prior art elastomeric compounds. The elastomeric compounds pref-

erably contain s-SBR as the elastomer, and may contain other polymers, preferably dienes. The elastomeric compounds can be used in any dynamic application, including but not limited to tire tread and motor mount applications.

The invention will now be described through illustrative examples. The examples are not intended to limit the scope of the invention defined in the appended claims.

EXAMPLE 1

A precipitated amorphous silica product in accordance with the invention was produced by combining 260 L of water and 200 L of 24.7% sodium silicate (3.3 silicate mole ratio, 82.9% excess silicate; excess silicate=100×volume of silicate initially present in the reaction medium÷total volume of silicate used in the reaction) in a reactor and heating the reaction medium to 82° C. To the heated reaction medium was added 9.5 kg of anhydrous sodium sulfate. Thereafter, sulfuric acid (7.4%) at 33° C. was introduced to the heated reaction medium at 4.5 L/min. When the reaction medium pH reached 7.5, the acid addition rate was slowed to 1.81 L/min, and an addition of 24.7% sodium silicate (3.3 mole ratio) at 1.38 L/min commenced. During the simultaneous addition, the precipitation pH was maintained at 7.5 by adjusting the acid addition rate. The silicate addition was terminated after 30 minutes, but the acid addition continued thereafter at 1.81 L/min until a reaction mixture pH of 5.1 was achieved. The reaction mixture was then allowed to digest at 82° C. for 10 minutes, after which the pH was readjusted to 5.1 with more acid.

Precipitated silica slurry was rotary-filtered from the reaction mixture and washed with water until the sodium sulfate content was reduced. Thereafter, the silica slurry was spray dried.

Physical characteristics of the final product were evaluated as follows, and are summarized in Table 1.

Average Particle Size (APS)

Particle size was determined using a Leeds and Northrup Microtrac II apparatus. During operation, a laser beam is projected through a transparent cell which contains a stream of moving particles suspended in a liquid. Light rays which strike the particles are scattered through angles which are inversely proportional to their sizes. The photodetector array measures the quantity of light at several predetermined angles. Electrical signals proportional to the measured light flux values are then processed by a microcomputer system to form a multi-channel histogram of the particle size distribution.

Multipoint BET

A Gemini III 2375 Surface Area Analyzer (Micromeritics Corporation) was used to determine the surface area of solid materials. During operation, an analysis gas (nitrogen) is metered simultaneously into a tube containing the sample and into a (blank) balance tube. The internal volume and the temperature surrounding both tubes are maintained at identical conditions, with the only difference being the presence of sample in the sample tube.

The sample and balance tubes are immersed in a single liquid nitrogen bath which maintains isothermal conditions for both tubes. Metering of the analysis gas is delivered to both the balance and sample tubes through separate servo valves. A differential pressure transducer measures the pressure imbalance between both tubes, which is caused by the adsorption of the gas onto the sample. As the sample adsorbs analysis gas, the servo valve maintains the pressure balance between the two tubes by admitting more gas into the sample tube. The end result is that the Gemini maintains a constant pressure of the analysis gas over the sample while varying the rate of analysis gas delivery to match the rate at which the sample can adsorb the gas.

Bulk Fines and Pellet Distribution of Compacted Products

Bulk Fines and Pellet Distribution of Compacted Products were determined by weighing fractions retained on or passing through 8 inch diameter stainless steel U.S. Sieves number 50 and 200 mesh, opening sizes 297 μm and 74 μm, respectively.

10.0±0.1 g of sample is placed on top of a stacked set of screens. The screens are covered and shaken for 5 minutes on a Portable Sieve Shaker, C-E Tyler Model RX-24, (W. S. Tyler Inc.). The percentage of the sample passing or retained on the mesh sizes of interest is determined by weight.

Granule Bulk Density (Loose or Pour Density of Compacted Product)

A funnel with an opening which can be closed is placed at a fixed height of 3 inches directly above the mouth of a standard pint cup. The granules are loaded into the closed funnel. The funnel is opened and the granules are free to fall into and overflow the cup. The granules are scraped off level with the top of the cup using the flat edge of a spatula. The full cup is weighed and the weight of the granules (in grams to the nearest 0.1 gram) is determined by subtracting the weight of the empty cup. The weight of the granules is divided by the standard volume (in mL) of the cup to give the bulk density in g/mL.

Pore Volume Method

Pore volume (mercury pore volume) is determined using an Autopore II 9220 Porosimeter (Micromeritics Corporation). This instrument measures the void volume and pore size distribution of various materials. Mercury is forced into the voids as a function of pressure and the volume of the mercury intruded per gram of sample is calculated at each pressure setting. Total pore volume expressed herein represent the cumulative volume of mercury intruded at pressures from vacuum to 60,000 psi. Increments in volume (cm^3/g) at each pressure setting are plotted against the pore radius corresponding to the pressure setting increments. The peak in the intruded volume versus pore radius curve corresponds to the mode in the pore size distribution and identifies the most common pore size in the sample.

Oil Absorption

Oil absorption, using linseed or DBP (dibutylphthalate) oil, was determined by the rub-out method. The method involves mixing linseed or DBP oil with a silica product by rubbing with a spatula on a smooth surface until a stiff putty-like paste is formed. By measuring the quantity of oil required to saturate the silica product, i.e. the quantity of oil required to form a silica/oil paste mixture which curls when spread out, the oil absorption of the silica product is determined. The oil absorption value is calculated as follows:

$$\text{Oil absorption}=(\text{cm}^3 \text{ oil absorbed}\times 100)\div\text{weight of silica product, grams}=\text{cm}^3 \text{ oil/100 grams silica product}$$

CTAB Surface Area

The external surface area of silica product was determined by adsorption of CTAB (cetyltrimethylammonium bromide) on the silica product surface, the excess CTAB being separated by centrifugation and determined by titration with sodium lauryl sulfate using a surfactant electrode. The external surface area of the silica product is calculated from the quantity of CTAB adsorbed (analysis of CTAB before and after adsorption).

Specifically, about 0.5 g of silica product is placed in a 250-mL beaker with 100.00 mL CTAB solution (5.5 g/L).

The solution is mixed on an electric stir plate for 1 hour then centrifuged for 30 minutes at 10,000 rpm. 1 mL of 10% Triton X-100 is added to 5 mL of the clear supernatant in a 100-mL beaker. The pH is adjusted to 3.0–3.5 with 0.1 N HCl and titrate with 0.0100 M sodium lauryl sulfate using a surfactant electrode (Brinkmann SUR15O1-DL) to determine the endpoint.

Projected Surface Area

The average projected area of the silica product is determined by the following method. 150 mg of silica product are introduced into a beaker containing a mixture of 10 mL of water and 20 mL of isopropyl alcohol; the mixture is agitated with ultrasonics (L&R-PC5 Ultrasonic Cleaning Systems) for 60 minutes, while maintaining temperature below 30° C. After which, while continuing the ultrasonic agitation, 10 microliters of the contents of the beaker are removed by a micropipet and placed on three 200-mesh copper grids which had been carbon Formvar coated. Excess liquid is removed by wicking (touching a sharp comer of filter paper to the drop) after allowing the drop to stand for 20 seconds, so as to prevent reagglomeration of the particles. The average projected area of 1000 aggregates is determined by image analysis.

For image analysis, the TEM micrographs were placed on the epidiascope attachment of the image analyzing computer. Using the area function, the area of all measurable particles in the micrographs was measured. Only particles whose entire feature lay in the micrographs and whose boundaries were clearly defined were analyzed. In this case, a particle was defined as an aggregate of silica particles. Various size ranges were selected according to the available ranges of the image analyzer. The data were obtained as the number of particles within each size range.

5% pH

A 5% pH is determined by weighing 5.0 grams of silica product into a 250-mL beaker, adding 95 mL deionized or distilled water, mixing for 7 minutes on a magnetic stir plate, and measuring the pH with a pH meter which has been standardized with two buffer solutions bracketing the expected pH range.

Percent Sodium Sulfate

A 13.3 gram sample of silica product is weighed out and added to 240 mL of distilled water. The slurry is mixed for 5 minutes on a Hamilton Beach mixer. The slurry is transferred to a 250 mL graduate and distilled water is added to make 250 mL of slurry. Sample is mixed and the temperature of the slurry is determined. The conductivity of the solution is measured using a Solu-Bridge with the temperature compensator properly adjusted. The percent sodium sulfate is determined from a standard calibrated chart.

Percent Moisture

A sample of about 2.0 grams is weighed in a pre-weighed weighing dish to the nearest 0.0001 gram. The sample is placed in an oven for 2 hours at 105° C., then removed and cooled in a desiccator. The cooled sample is weighed and the weight loss is divided by the original weight of sample and multiplied by 100, resulting in the percent moisture.

EXAMPLE 2

A precipitated amorphous silica product in accordance with the invention was produced by combining 235 L of water and 166 L of 30.0% sodium silicate (2.5 silicate mole ratio, 84.7% excess silicate) in a reactor and heating the reaction medium to 87° C. Sulfuric acid (11.4%) at 33° C. was introduced to the heated reaction medium at 2.7 L/min. When the reaction medium pH reached 7.5, the acid addition rate was slowed to 1.4 L/min, and an addition of 30.0% sodium silicate (2.5 mole ratio) at 1.0 L/min commenced. During the simultaneous addition, the precipitation pH was maintained at 7.5 by adjusting the acid addition rate. The silicate addition was terminated after 30 minutes, but the acid addition continued thereafter at 1.3 L/min until a reaction mixture pH of 5.5 was achieved. The reaction mixture was then allowed to digest at 87° C. for 10 minutes, after which the pH was readjusted to 5.5 with more acid.

Precipitated silica slurry was rotary-filtered from the reaction mixture and washed with water until the sodium sulfate content was reduced. The pH of the washed silica slurry was adjusted to 6.5 with more acid, and thereafter the silica slurry was spray dried.

The physical properties of the final product were measured as described in Example 1, and the results are summarized in Table 1.

EXAMPLE 3

A precipitated amorphous silica product in accordance with the invention was produced by combining 2568 gal. of 1.8% sodium sulfate and 1707 gal. of 24.7% sodium silicate (3.3 silicate mole ratio, 76.4% excess silicate) in a reactor and heating the reaction medium to 180° F. Sulfuric acid (7.4%) at 90° F. was then introduced into the heated reaction medium at 34.0 gal./min. When the reaction medium pH reached 7.8, the acid addition rate was slowed to 17.6 gal./min, and an addition of 24.7% sodium silicate (3.3 mole ratio) at 11.9 gal./min commenced. During the simultaneous addition, the precipitation pH was maintained at 7.3–7.7 by adjusting the acid addition rate. The silicate addition was terminated after 30 minutes, but the acid addition continued thereafter at 17.6 gal./min until a reaction mixture pH of 5.5 was achieved. The reaction mixture was then allowed to digest at 180° F. for 10 minutes, after which the pH was readjusted to 5.5 with more acid.

Precipitated silica slurry was rotary-filtered from the reaction mixture and washed with water until the sodium sulfate content was reduced. Thereafter, the silica slurry was spray dried.

The physical properties of the final product were measured as described in Example 1, and the results are summarized in Table 1.

EXAMPLE 4

A silica product was prepared as described in Example 2, then granulated. Granulation was accomplished by compacting the silica product between pocketed tandem rolls at 700 psi, then attriting the compacted silica product into smaller particles. The fine fraction (less than 16 mesh) of the smaller particles was recycled into the tandem rolls along with additional silica product to produce a denser compacted silica product, which was then attrited and screened to produce a granulated silica product having a granule bulk density of 0.281 g/mL and a size distribution of 83.3% +50 mesh and 5.4% −200 mesh. Prior to and during compaction, vacuum was applied to the granulation system to deaerate the silica feed.

The physical properties of the final product were measured as described in Example 1, and the results are summarized in Table 1.

EXAMPLE 5

A precipitated amorphous silica product in accordance with the invention was produced by combining 2732 gal. of water and 1749 gal. of 30% sodium silicate (2.5 silicate mole

ratio, 83.6% excess silicate) in a reactor and heating the reaction medium to 87° C. Sulfuric acid (11.4%) at 33° C. was then introduced into the heated reaction medium at 30.2 gal./min. When the reaction medium pH reached 7.5, the acid addition rate was slowed to 15.6 gal./min, and an addition of 30% sodium silicate (2.5 mole ratio) at 11.4 gal./min commenced. During the simultaneous addition, the precipitation pH was maintained at 7.5 by adjusting the acid addition rate. The silicate addition was terminated after 30 minutes, but the acid addition continued thereafter at 14.5 gal./min until a reaction mixture pH of 5.5 was achieved. The reaction mixture was then allowed to digest at 87° C. for 10 minutes, after which the pH was readjusted to 5.5 with more acid.

Precipitated silica slurry was rotary-filtered from the reaction mixture and washed with water until the sodium sulfate content was reduced. Thereafter, the silica slurry was spray dried, and the spray dried silica product was granulated as described in Example 4 except that a tandem rolls of 200 psi was used, and no vacuum was applied to the system.

The physical properties of the final product were measured as described in Example 1, and the results are summarized in Table 1.

EXAMPLE 6

A precipitated amorphous silica product in accordance with the invention was produced by combining 3041 gal. of water and 1692 gal. of 30% sodium silicate (2.5 silicate mole ratio, 83.2% excess silicate) in a reactor and heating the reaction medium to 78° C. Sulfuric acid (11.4%) at 33° C. was then introduced into the heated reaction medium at 29.3 gal./min. When the reaction medium pH reached 7.5, the acid addition rate was slowed to 15.6 gal./min, and an addition of 30% sodium silicate (2.5 mole ratio) at 11.4 gal./min commenced. During the simultaneous addition, the precipitation pH was maintained at 7.5 by adjusting the acid addition rate. The silicate addition was terminated after 30 minutes, but the acid addition continued thereafter at 15.6 gal./min until a reaction mixture pH of 5.3 was achieved. The reaction mixture was then allowed to digest at 78° C. for 10 minutes, after which the pH was readjusted to 5.3 with more acid.

Precipitated silica slurry was rotary-filtered from the reaction mixture and washed with water until the sodium sulfate content was reduced. The pH of the washed silica slurry was adjusted to 6.5 with more acid as needed, and thereafter the silica slurry was spray dried.

The physical properties of the final product were measured as described in Example 1, and the results are summarized in Table 1.

EXAMPLE 7

A silica product was prepared as described in Example 6, then granulated as described in Example 4, except a tandem roll pressure of 620 psi was used, and no vacuum was applied to the system.

The physical properties of the final product were measured as described in Example 1, and the results are summarized in Table 1.

In addition to the above-described Examples, the physical properties of three commercially-available precipitated amorphous silica products were tested as described in Example 1, and the results are summarized in Table 2. Comparative Example 1 is Zeofree® 80 (J.M. Huber Corporation), Comparative Example 2 is Zeosil® 1165MPND (Rhone-Poulenc Chimie), and Comparative Example 3 is Zeopol® 8741 (J.M. Huber Corporation).

TABLE 1

Physical Characteristics	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Form	Powder	Powder	Powder	Granules	Granules	Powder	Granules
Specific Surface Area by CTAB, m^2/g	87	55	114	61	76	93	95
Specific Surface Area by BET, m^2/g	133	75	150	83	91	132	187
5% pH	6.9	7.0	7.0	7.0	7.4	6.9	6.9
Mercury Intrusion Peak Diameter Location, Å	640	1020	360	640	790	610	500
Mercury Intrusion Total Pore Volume, cm^3/g	4.2676	3.7618	4.5191	1.8637	5.5669	4.8330	2.6777
Mercury Intrusion Pore Volume Ratio V2/V1)*100	20.4	21.2	28.6	23.8	19.2	23.4	23.6
Granule Bulk Density g/mL	****	****	****	0.281	0.197	****	0.225
% Na_2SO_4	1.3	1.2	1.5	1.3	2.6	1.3	1.8
APS MicroTrac for Powders, microns	54.2	28.6	66.6	****	****	62.5	****
Projected Surface Area, nm^2	3098	****	****	****	****	****	****
% Retained on 50 Mesh for Granules	****	****	****	83.3	81.2	****	91.8
% Thru 200 Mesh for Granules	****	****	****	5.4	5.6	****	3.4
% Free Moisture	5.3	5.0	4.7	5.7	6.8	5.9	5.3
Linseed Oil Absorption, $cm^3/100$ gram	204	218	233	203	169	210	177

TABLE 1-continued

Physical Characteristics	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
DBP Oil Absorption, cm^3/100 gram	210	248	248	229	202	242	205

TABLE 2

Physical Characteristics	Comparative Example 1	Comparative Example 2	Comparative Example 3
Trade name	Zeofree ® 80	Zeosil ® 1165	Zeopol ® 8741
Form	Powder	Micro-pearls	Powder
Specific Surface Area by CTAB m^2/g	55	153	143
Specific Surface Area by BET m^2/g	85	164	183
5% pH	7.0	6.4	7.2
Mercury Intrusion Peak Diameter Location, A	700	250	285
Mercury Intrusion Total Pore Volume, cm^3/g	19.9	3.0799	4.9975
Mercury Intrusion Pore Volume Ratio (V2/V1)*100	81.0	56.6	39.7
% Na_2SO_4	1.9	0.51	1.8
APS MicroTrac microns for Powders	14.2	268	45
% Free Moisture	5.7	5.5	5.0
Projected Surface Area, nm^2	4211	9627	1967
Linseed Oil Absorption, cm^3/100 gram	202	185	185
DBP Oil Absorption, cm^3/100 gram	222	233	298

Each of the inventive silica products described in Table 1 and the prior art silica products described in Table 2 was then incorporated at various loadings into identical rubber matrices to compare the characteristics imparted by the silica products to rubber compounds. In addition, a rubber compound was prepared using carbon black filler (no silica filler/no coupling agent). The composition of the rubber matrix is described in Table 3, while the exact silica forms (powder or granulated) and loading levels are provided in Table 4. The resulting rubber compounds were evaluated in accordance with industry standards for Mooney Viscosity (ASTM D1646), Mmax (ASTM D2084), t_{s2} (ASTM D2084), T90 (ASTM D2084), 100, 200 and 300% modulus (ASTM D412), Tensile at Break (ASTM D412), Elongation at Break (ASTM D412), Molded Groove Tear Strength (ASTM D624), DIN Abrasion Resistance (ISO-4649 Method B), NBS Abrasion Resistance Rating (ASTM D1630), Firestone Running Temperature (ASTM D623), Zwick Rebound at −25, 22 and 100° C. (ASTM 1504), and 1% and 12% DSA Tangent Delta at 60° C. (measured on an RPA 2000 by Monsanto). The results are summarized in Table 4.

TABLE 3

Ingredient	Carbon Black N-234 Formula	Silica Formulas
Solution SBR-JSR-SL574*	75	75
Polybutadiene CB11**	25	25
Reinforcing Filler	80	80
Stearic Acid	1	1
Coupling Agent X-50S	0	00.0–12.80
Sundex 8125	32.5	32.5
Zinc Oxide	2.5	2.5
Sunolite 240TG***	1.5	1.4
Santoflex 13	2	2
Sulfur	1.35	1.7
Delac S	1.35	1.7
DPG	0	2
Total phr	222.2	224.80–237.60

*Japanese Synthetic Rubber Company
**Bayer Fibers, Organics & Rubber Division
***Sovereign Chemical Company

TABLE 4

Rubber Physical and Performance Characteristics	Rubber with N-234 Carbon Black	Rubber with Comp. Ex. 1 Filler	Rubber with Comp. Ex. 2 Filler	Rubber with Comp. Ex. 2 Filler	Rubber with Comp. Ex. 3 Filler	Rubber with Comp. Ex. 3 Filler	Rubber with Ex. 1 Filler	Rubber with Ex. 1 Filler	Rubber with Ex. 3 Filler	Rubber with Ex. 5 Filler	Rubber with Ex. 6 Filler	Rubber with Ex. 7 Filler
Form of Silica Filler	***	Powder	Micropearls	Micropearls	Powder	Powder	Powder	Powder	Powder	Granules	Powder	Granules
Coupling Agent (phr)	0.00	7.20	12.80	8.96	12.80	8.96	12.8	7.20	10.0	7.00	7.0	7.0
Mmax (Nm)	6.5	7.9	9.0	8.5	8.0	7.6	8.9	7.3	8.1	6.9	8.0	9 6
t_{s2} (min)	3.8	2.2	1.9	1.8	1.9	1.7	1.9	2.3	2.2	2.3	2.8	2 5
T90 (min)	7.3	3.8	9.3	13.0	6.4	9.3	5.5	4.7	6.8	4.0	5.5	5 6
Mooney Viscosity $M_{L(1+4)}$ @ 100 C (mu)	70.9	50.0	92.0	97.0	82.0	86.0	57.2	59.4	72.5	49.3	50.8	60.3
100% Modulus (MPa)	2.01	2.74	2.90	2.53	2.85	2.30	3.94	2.45	2.94	2.64	2.63	2.87
200%	4.31	6.98	7.03	6.17	8.24	6.34	10.7	6.50	7.10	7.36	6.13	6.95

TABLE 4-continued

Rubber Physical and Performance Characteristics	Rubber with N-234 Carbon Black	Rubber with Comp. Ex. 1 Filler	Rubber with Comp. Ex. 2 Filler	Rubber with Comp. Ex. 2 Filler	Rubber with Comp. Ex. 3 Filler	Rubber with Comp. Ex. 3 Filler	Rubber with Ex. 1 Filler	Rubber with Ex. 1 Filler	Rubber with Ex. 3 Filler	Rubber with Ex. 5 Filler	Rubber with Ex. 6 Filler	Rubber with Ex. 7 Filler
Modulus (MPa) 300% Modulus (MPa)	8.07	12.7	14.4	12.0	13.2	13.1	***	12.1	9.24	13.2	10.5	12 0
Tensile at Break (MPa)	18.9	15.4	17.8	16.8	18.2	19.1	14.4	16.4	15.0	15.6	14.3	14.8
% Elongation at Break	618	341	346	371	367	386	251	372	344	344	384	346
DIN Abrasion Resistance Index	***	***	112	102	134	129	***	***	***	127	136	123
NBS Abrasion Resistance Rating (%)	4190	4392	9500	11500	9060	11300	9928	11065	7041	***	***	8082
Firestone Running Temperature, C	150	94	104	107	99	102	97	94	100	***	***	***
Zwick Rebound @ 100 C (%)	50	73	65	63	68	67	62	70	70	79	70	69
Zwick Rebound @ 22 C (%)	35	63	50	51	54	55	60	58	56	62	57	61
Zwick Rebound @ -25 C (%)	11.0	7.6	7.6	7.6	6.6	6.8	6.4	8.4	7.6	5.8	7.8	7 0
Tan Delta 60 C 12% DSA	0.353	0.087	0.155	0.139	0.110	0.110	0.101	0.102	0.118	0.100	***	***
Tan Delta 60 C 1% DSA	0.289	0.057	0.118	0.103	0.090	0.079	0.084	0.086	0.098	0.064	***	***

More silica products in accordance with the invention were prepared in accordance with Example 6 and utilizing the silicate specific gravity, excess silicate, reaction temperature, digestion temperature and spray dryer feed pH noted in Table 5. These inventive silica products were individually incorporated into a rubber formulation described in Table 6, as was a prior art silica product for comparative purposes (Zeopol® 8745, J.M. Huber Corporation). The resulting rubber formulations were tested in accordance with passenger tire industry standards (as described above in association with Table 4), and the results are summarized in Table 7.

TABLE 5

Synthesis Parameters, Physical Characteristics	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14	Example 15
Form	Powder	Powder	Powder	Powder	Powder	Powder	Powder	Powder
Silicate Specific Gravity in Reaction Medium	1.120	1.120	1.135	1.135	1.135	1.135	1.135	1.135
Excess Silicate, %	83.7	83.7	83.7	83.7	83.7	83.7	83.7	83.7
Reaction Temperature, ° C.	80	80	80	80	68	68	68	68
Digest Temperature, ° C.	80	80	80	80	68	68	93	93
Spray Dryer Feed pH	6.8	6.2	6.8	6.2	6.8	6.2	6.8	6.2
Specific Surface Area by CTAB, m^2/g	80	90	72	72	118	119	104	110
Specific Surface Area by BET, m^2/g	120	152	130	153	243	261	170	220
5% pH	7.35	6.87	7.14	7.25	7.48	6.99	7.2	7.1
Mercury Intrusion Peak Diameter Location, Å	590	580	850	830	450	420	400	410
Mercury Intrusion Total Pore Volume, cm^3/g	4.7917	4.3743	4.4631	4.3070	4.4379	4.4070	4.5979	3.4736
Mercury Intrusion Pore Volume Ratio (V2/V1)*100	24.2	22.2	24.9	21	32.6	32.9	30.7	31.9
% Na_2SO_4	2.32	1.14	2.39	1.06	1.29	1.14	4.28	1.61
APS MicroTrac,	46.4	43.0	58.6	55.8	84.1	49.3	66.6	56.8

TABLE 5-continued

Synthesis Parameters, Physical Characteristics	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14	Example 15
microns								
% Free Moisture	4.7	4.7	5.1	4.5	6.6	5.8	5.0	4.4
Linseed Oil Absorption, $cm^3/100$ gram	235	225	218	214	245	237	237	242
DBP Oil Absorption, $cm^3/100$ gram	251	268	231	241	279	272	256	255

TABLE 6

Ingredient	Silica Formulas
Solution - SBR	70.00
Polybutadiene	30.00
Reinforcing Filler	70.00
Coupling Agent X-50S	11.00
Processing Aids	33.50
Sulfur	1.70
Cure Agents	9.20
Total phr	225.10

equal to or better than the rubber compounds containing the prior art silica products in every evaluated performance characteristic. The Tables also show that the inventive silica products compare very favorably to the previously used carbon black filler as reflected by the rubber performance characteristics. More specifically, the inventive silica products exhibited yielded rubber compound having all of the same advantages of rubber compounds filled with prior art silica products while increasing the benefits of abrasion resistance. The inventive silica products also enhanced the processability of the rubber compounds over the prior art highly-dispersible silica fillers to levels achieved with carbon black fillers. Moreover, the Tables show that the new

TABLE 7

Performance Characteristic	Rubber with Zeopol ® 8745 Filler	Rubber with Example 8 Filler	Rubber with Example 9 Filler	Rubber with Example 10 Filler	Rubber with Example 11 Filler	Rubber with Example 12 Filler	Rubber with Example 13 Filler	Rubber with Example 14 Filler	Rubber with Example 15 Filler
Form	Granule	Powder	Powder	Powder	Powder	Powder	Powder	Powder	Powder
Mmax (Nm)	64.6	65.6	66.3	67.0	68.0	65.4	65.0	66.1	67.1
t_{s2} (min)	5.0	4.0	4.2	3.8	3.8	4.8	4.4	4.6	4.9
T90 (min)	12.1	7.1	7.4	7.0	8.3	10.1	14.4	9.9	13.6
Mooney Viscosity $M_{L(1+4)}$ @ 100 C (mu)	81.0	81.7	84.2	81.0	81.7	84.8	91.3	88.7	92.9
100% Modulus (MPa)	2.26	2.57	2.62	2.59	3.02	2.43	2.46	2.52	2.67
200% Modulus (MPa)	6.67	6.94	7.33	6.99	7.80	6.33	6.73	6.92	7.75
300% Modulus (MPa)	13.4	12.7	13.5	12.7	13.5	12.1	12.8	13.2	14.8
Tensile at Break (MPa)	21.7	18.9	19.2	16.8	17.0	19.3	19.5	19.6	18.3
% Elongation at Break	420	399	393	378	364	421	395	401	360
Tear - Molded Groove (kN/m)	46	25	27	25	25	47	47	36	31
Tan Delta @ 60 C 12% DSA	0.128	0.104	0.102	0.090	0.099	0.113	0.119	0.111	0.112
Tan Delta @ 60 C 1% DSA	0.078	0.066	0.062	0.061	0.065	0.074	0.078	0.073	0.073

Table 8 summarizes the relative performances of the silica products as reflected by the rubber characteristics listed in Tables 4 and 7. Tables 4, 7 and 8 reveal that the rubber compounds containing the inventive silica products perform silica products as rubber fillers have reduced coupling agent demand, lower heat build-up, and improved wet/ice traction over both carbon black and the prior art silica products.

TABLE 8

Performance Characteristics	Preferred Values	Inventive Example Silica Products versus Carbon Black	Granulated Inventive Example Silica Products versus Comparative Example 1	Inventive Example Silica Products versus Comparative Examples 2 and 3
Form	Granules	Equal	Much Superior	Equal/Better
Coupling Agent (Si-69) loading	Lower/Cost	Poorer	Better	Much Superior
Mmax (Nm)	Greater	Poorer	Equal/Better	Equal
t_{s2} (min)	Greater	Poorer	Equal	Better
T90 (min)	Lower	Better	Equal	Better
Mooney Viscosity $M_{L(1+4)}$ @ 100° C. (mu)	Lower/Processing	Better	Equal/Poorer	Much Superior
100% Modulus (MPa)	Lower	Poorer	Equal	Equal
200% Modulus (MPa)	Greater	Better	Equal	Equal
300% Modulus (MPa)	Greater	Better	Equal	Equal/Better
Tensile at Break (MPa)	Greater	Poorer	Equal	Equal
% Elongation at Break	Greater	Poorer	Equal	Equal
NBS Abrasion Resistance Rating (%)	Greater	Much Superior	Much Superior	Equal
Firestone Running Temp (° C.)	Lower	Much Superior	Equal	Much Superior
Zwick Rebound @ 100° C. (%)	Greater	Much Superior	Equal	Equal
Zwick Rebound @ 22° C. (%)	Greater	Much Superior	Equal	Equal
Zwick Rebound @ -25° C. (%)	Lower	Much Superior	Equal/Better	Equal/Better
Tan Delta @ 60° C. 12% DSA	Lower	Much Superior	Equal	Much Superior
Tan Delta @ 60° C. 1% DSA	Lower	Much Superior	Equal	Much Superior

The examples factually demonstrate that the invention provides unexpectedly improved processing and performance characteristics in rubber compounds for tire treads. In particular, the invention provides a highly-advantageous combination of performance characteristics to rubber tire tread formulations previously thought to be contradictory, such as reduced rolling resistance (evidenced by the low Firestone Running Temperature, high Zwick 100° C. rebound, and low Tan Delta at 60° C.), improved traction over a wide range of conditions (evidenced by the low Zwick rebound at −25° C.), and excellent abrasion resistance (evidenced by the NBS abrasion resistance values).

Rubber mixing and extrusion advantages provided by the invention are evidenced by the low Mooney viscosity values seen above. Further, the low T90 (associated with increased production rates) and high t_{s2} (scorch) values demonstrates that processing improvements are obtained with the invention without premature setting of the composition.

While the invention has been described herein with reference to specific and preferred embodiments, it is understood that changes, modifications, substitutions and omissions may be made without departing from the spirit and scope of the invention defined in the appended claims.

We claim:

1. A precipitated amorphous silica product comprising:
   - a CTAB specific surface area of about 10 m^2/g to less than 140 m^2/g;
   - a multi-point BET surface area of about 50–261 m^2/g;
   - a 5% pH value of about 5.0–8.5;
   - a DBP oil absorption of about 160–310 $cm^3/100$ g;
   - a linseed oil absorption of about 150–300 $cm^3/100$ g;
   - a projected surface area of no greater than about 4000 nm^2; and
   - a pore volume ratio of pores ranging from 175 to 275 Å in diameter to all pores less than 400 Å in diameter of about 10% to less than 50%.

2. The precipitated amorphous silica product according to claim 1, wherein said CTAB specific surface area is about 10–110 m^2/g.

3. The precipitated amorphous silica product according to claim 1, wherein said CTAB specific surface area is about 10 m^2/g to less than 100 m^2/g.

4. The precipitated amorphous silica product according to claim 3, wherein said projected surface area is no greater than 3500 nm^2.

5. A formed precipitated amorphous silica product comprising:
   - a CTAB specific surface area of about 10 m^2/g to less than 140 m^2/g;
   - a multi-point BET surface area of about 50–261 m^2/g;
   - a 5% pH value of about 5.0–8.5;
   - a DBP oil absorption of about 160–310 $cm^3/100$ g;
   - a linseed oil absorption of about 150–300 $cm^3/100$ g;
   - a projected surface area of no greater than about 4000 nm^2; and
   - a pore volume ratio of pores ranging from 175 to 275 Å in diameter to all pores less than 400 Å in diameter of about 10% to less than 50%.

6. The formed precipitated amorphous silica product according to claim 5, wherein said CTAB specific surface area is about 10–110 m^2/g.

7. The formed precipitated amorphous silica product according to claim 5, wherein said CTAB specific surface area is about 10 m^2/g to less than 100 m^2/g.

8. The formed precipitated amorphous silica product according to claim 5, further comprising a bulk density of about 0.16–0.30 g/mL.

9. The formed precipitated amorphous silica product according to claim 5, further comprising a bulk density of about 0.16–0.27 g/mL.

10. The formed precipitated amorphous silica product according to claim 5, further comprising a minus 200 mesh content of no greater than about 20 wt %.

11. The formed precipitated amorphous silica product according to claim **10**, wherein said minus 200 mesh content is no greater than about 10 wt %.

12. A method of producing a precipitated amorphous silica product, comprising the steps of:

(a) adding an acid to a mixture of water and an alkaline metal silicate at a substantially constant rate until a reaction mixture having a pH of about 10.0–6.5 is formed, said mixture being at a temperature of about 60–90° C., and said silicate having a mole ratio of about 2.4–3.3;

(b) adding more of said silicate to said reaction mixture for about 0–60 minutes while simultaneously controlling said rate of acid addition to maintain said reaction mixture pH at about 10.0–6.5;

(c) discontinuing said silicate addition and continuing said acid addition until a reaction mixture pH to about 4.5–6.5 is achieved;

(d) digesting said reaction mixture for about 0–60 minutes at a temperature of about 60–99° C.;

(e) filtering said reaction mixture to recover a silica slurry;

(f) washing said silica slurry to form a washed silica product; and

(g) drying said washed silica product to form a dried silica product.

13. The method according to claim **12**, wherein said washing step is performed until said washed silica product has a sodium sulfate content of no greater than about 4.5%.

14. The method according to claim **12**, further comprising the step of adjusting the pH of said washed silica product to about 6.0–7.0.

15. The method according to claim **12**, wherein said drying step is performed until said dried silica product has an H_2O content of no greater than about 8%.

16. The method according to claim **12**, wherein an electrolyte is added during at least one of said steps selected from the group consisting of adding an acid to a mixture of water and an alkaline metal silicate, adding more of said silicate to said reaction mixture, discontinuing said silicate addition and continuing said acid addition, and digesting said reaction mixture.

17. The method according to claim **16**, wherein said electrolyte is sodium sulfate.

18. An elastomeric compound comprising an elastomer and a precipitated amorphous silica product, said silica product comprising:

a CTAB specific surface area of about 10 m^2/g to less than 140 m^2/g;

a multi-point BET surface area of about 50–261 m^2/g;

a 5% pH value of about 5.0–8.5;

a DBP oil absorption of about 160–310 $cm^3/100$ g;

a linseed oil absorption of about 150–300 $cm^3/100$ g;

a projected surface area of no greater than about 4000 nm^{2}; and

a pore volume ratio of pores ranging from 175 to 275 Å in diameter to all pores less than 400 Å in diameter of about 10% to less than 50%.

19. The elastomeric compound according to claim **18**, wherein said CTAB specific surface area of said silica product is about 10–110 m^2/g.

20. The elastomeric compound according to claim **18**, wherein said CTAB specific surface area of said silica product is about 10 m^2/g to less than 100 m^2/g.

21. The elastomeric compound according to claim **18**, wherein said precipitated amorphous silica product is a formed silica product.

22. The elastomeric compound according to claim **21**, wherein said formed silica product has a bulk density of about 0.16–0.30 g/mL.

23. The elastomeric compound according to claim **21**, wherein said formed silica product has a bulk density of about 0.16–0.27 g/mL.

24. The elastomeric compound according to claim **21**, wherein said formed silica product has a minus 200 mesh content of no greater than 20 wt %.

25. The elastomeric compound according to claim **18**, wherein said elastomer is a solution styrene-butadiene rubber.

26. The elastomeric compound according to claim **25**, wherein said elastomer further comprises at least one other polymer.

27. The elastomeric compound according to claim **26**, wherein said other polymer is a diene.

28. A passenger tire tread comprising an elastomer and a precipitated amorphous silica product, said silica product comprising:

a CTAB specific surface area of about 10 m^2/g to less than 140 m^2/g;

a multi-point BET surface area of about 50–261 m^2/g;

a 5% pH value of about 5.0–8.5;

a DBP oil absorption of about 160–310 $cm^3/100$ g;

a linseed oil absorption of about 150–300 $cm^3/100$ g;

a projected surface area of no greater than about 4000 nm^{2}; and

a pore volume ratio of pores ranging from 175 to 275 Å in diameter to all pores less than 400 Å in diameter of about 10% to less than 50%.

29. The passenger tire tread according to claim **28**, wherein said CTAB specific surface area of said silica product is about 10–110 m^2/g.

30. The passenger tire tread according to claim **28**, wherein said CTAB specific surface area of said silica product is about 10 m^2/g to less than 100 m^2/g.

31. The passenger tire tread according to claim **28**, wherein said silica product is a formed silica product.

32. The passenger tire tread according to claim **31**, wherein said formed silica product has a bulk density of about 0.16–0.30 g/mL.

33. The passenger tire tread according to claim **31**, wherein said formed silica product has a bulk density of about 0.16–0.27 g/mL.

34. The passenger tire tread according to claim **31**, wherein said formed silica product has a minus 200 mesh content of no greater than about 20 wt %.

35. The passenger tire tread according to claim **28**, wherein said elastomer is a solution styrene-butadiene rubber.

36. The passenger tire tread according to claim **35**, wherein said elastomer further comprises at least one other polymer.

37. The passenger tire tread according to claim **36**, wherein said other polymer is a diene.

* * * * *

RELATED PROCEEDINGS APPENDIX

None.